

Formation of Primary Amines on Silicon Nitride Surfaces: a Direct, Plasma-Based Pathway to Functionalization

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Silicon nitride is the most commonly used passivation layer in biosensor applications where electronic components must be interfaced with ionic solutions. Unfortunately, the predominant method for functionalizing silicon nitride surfaces, silane chemistry, suffers from a lack of reproducibility. As an alternative, we have developed a silane-free pathway that allows for the direct functionalization of silicon nitride through the creation of primary amines formed by exposure to a radio frequency glow discharge plasma fed with humidified air. The aminated surfaces can then be further functionalized by a variety of methods; here we demonstrate using glutaraldehyde as a bifunctional linker to attach a robust NeutrAvidin (NA) protein layer. Optimal amine formation, based on plasma exposure time, was determined by labeling treated surfaces with an amine-specific fluorinated probe and characterizing the coverage using X-ray photoelectron spectroscopy (XPS). XPS and radiolabeling studies also reveal that plasma-modified surfaces, as compared with silane-modified surfaces, result in similar NA surface coverage, but notably better reproducibility.

Introduction

Silicon nitride films are widely used as surface layers in the electronics industry because of their utility as etch stops and their highly inert nature, including their ability to inhibit the penetration of contaminants such as water, oxygen, and ionic species.¹ Their inherent impermeability has also made silicon nitride films a surface of interest for various biosensing^{2,3} and bioMEMS⁴ devices. Biosensor applications require that the device be brought into contact with aqueous saline solutions, and silicon nitride films have proven to be robust and reliable for protecting such devices from solutions that would otherwise render them inoperable. Silicon nitride is also widely used in conjunction with silicon oxide in the production of planar waveguides for biosensing applications.⁵ In light of the sizable array of bio-related applications, a robust and reliable method for functionalizing silicon nitride surfaces with biomolecules would prove quite valuable.

The most prevalent method for functionalizing silicon nitride is to oxidize the surface and perform silanization chemistry that includes a functional terminal group which, in turn, is used for covalent attachment of a biomolecular film.^{3,5,6} Whereas silanization has proven useful, silane chemistry is notoriously inconsistent even under rigorous controls.^{7–10} Small variations

in the amount of water present during the silanization reaction can dramatically alter the thickness of the final film.^{11–13} Therefore, a more reliable and reproducible method for attaching biomolecules is desired. Arafat et al.¹⁴ achieved direct coupling of organic films to silicon nitride surfaces through the reaction of unsaturated carbon bonds with surface Si–H groups, but this can only be achieved on “silicon rich” (i.e., nonstoichiometric) silicon nitride. The harsh reaction conditions that are required (24 h at 165 °C) also make it unlikely that a monolayer could be formed with a functional end group that would survive the deposition process.

In surveying the available literature on silicon nitride, the presence of N–H bonds in the IR spectra of the bulk material has been noted on multiple occasions^{15–19} as being a remnant of the film growth process. Oxidation studies^{20–24} have also shown that N–H bonds can be formed in the bulk of otherwise stoichiometric silicon nitride using thermal oxidation in the

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presence of a hydrogen source (such as water). Habraken and Kuiper^{24,25} have gone as far as to suggest that N–H bond formation is required as an intermediate for silicon nitride oxidation, noting the similarity in bonding structure between Si–NH–Si and Si–O–Si matrices and the observation that oxidation does not occur in pure silicon nitride at low temperatures without the presence of a hydrogen source. Work with silicon nitride powders has further demonstrated that these N–H bonds can present themselves at the interface between the material and its surrounding media, affecting such bulk properties as ζ potential²⁶ and electrokinetic adsorption of ionic species.^{27–29} Despite the large body of work in this area and the potential uses of silicon nitride in various biological applications, the possibility of using these amino groups as coupling sites for biofunctionalization has not been seriously explored. Karymov and colleagues³⁰ claimed to have developed a method for direct coupling of DNA to surface amines and/or hydroxyls on silicon nitride using a bifunctional linker, but no controls were performed to show that the DNA was actually covalently immobilized. In fact, the density of DNA observed on the surfaces in question was consistent with that seen by Dugas and colleagues³¹ for DNA physisorbed on silicon oxide surfaces and was a full order of magnitude lower than that observed following covalent immobilization using bifunctional silane films. To our knowledge, there is no well-characterized method for directly creating stable surface amines and subsequent biofunctionality on silicon nitride.

In this paper, we present a method for aminating silicon nitride suitable for covalently coupling proteins to the surface using glutaraldehyde (GA) as a bifunctional linker. The creation of surface amine groups by reaction in a radio frequency glow discharge plasma fed with humidified air was examined by reaction with an amine-specific molecular label, fluorinated benzaldehyde, and characterized by X-ray photoelectron spectroscopy (XPS). We demonstrated that NeutrAvidin (NA) can be attached through the bifunctional linker, GA, by labeling the surface with a biotinylated fluorophore. The surface density of the immobilized protein was quantitatively measured by radio-labeling. Finally, direct comparisons are made between plasma-treated surfaces and amino-terminated silane films with respect to reproducibility and the surface density of the immobilized protein.

Materials and Methods

Materials. Silicon wafers and standard glass microscope slides sputter-coated with 5 nm of silicon nitride were purchased from Lance Goddard Associates (Foster City, CA). Glutaraldehyde, 4-(trifluoromethyl)benzaldehyde (TFMB), aminopropyltrimethoxysilane (APTMS), biotinylated Atto 647, and biotin were purchased from Sigma-Aldrich (St. Louis, MO). NeutrAvidin was purchased from Pierce (Rockford, IL). Tritium (³H)-labeled biotin was purchased from American Radiolabeled Chemicals (St. Louis, MO). Plasma cleaning for the nitride surfaces was done using a Mercator Control Systems LF-5 radio frequency (35 kHz) glow discharge plasma system. XPS analysis was performed using a Thermo (Waltham, MA) VG Scientific Escalab 220i-XL XPS system. The β -emissions of the tritium were counted by a Beckman (Fullerton, CA) LS 6500

Multi-purpose Scintillation Counter. Surface roughness was measured using a ThermoMicroscopes (Sunnyvale, CA) Autoprobe CP atomic force microscope (AFM). Fluorescent images were obtained using a Packard ScanArray Light confocal microarray scanner (Packard Biochip Technologies, Billerica, MA).

Surface Preparations. Silicon nitride-coated Si wafers were cleaned for 5 s in 1% hydrofluoric acid, then rinsed in 18 M Ω ·cm Nanopure water and dried with flowing nitrogen. Where appropriate, samples were then placed in the plasma chamber and cleaned with humidity-controlled air plasma for the allotted time at a power of 135 W and a pressure of 250 mTorr. Humidified air was produced by splitting a compressed air tank feed through a bubbler and desiccant bed and recombining the feeds at a ratio to provide 70% relative humidity. Dry air was run through a desiccant only (<1% relative humidity). Silicon oxide control samples were prepared by identical procedures using silicon wafers with a native oxide as substrates for XPS studies and standard glass microscope slides for imaging spots of fluorescently labeled biotin. To prepare silane films, silicon nitride-coated wafers were cleaned for 5 s in hydrofluoric acid, rinsed with Nanopure water, and then immersed in piranha solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 30 min. The samples were then rinsed in Nanopure water, dried with nitrogen, and transferred into a nitrogen glovebox. In the glovebox, they were immersed in a 5% solution of APTMS in absolute ethanol for 24 h. After this time, the samples were removed, rinsed with ethanol, and dried with nitrogen. This protocol for silane deposition was chosen because dry or nearly dry conditions are more likely to result in near-monolayer silane coverage.^{11,12} Keeping the coverage low is important—thick silane multilayers will obscure the underlying substrate surface and prevent quantitative XPS analysis.

Fluorine Labeling, XPS Analysis, and Surface Roughness. In order to determine the relative density of surface amine groups, samples were immersed in an 11% solution of TFMB in hexane for 2 h at room temperature. The TFMB concentration and exposure time were optimized to maximize labeling efficiency while limiting nonspecific physisorption. This optimization was accomplished by exposing samples of plasma-treated silicon nitride, as well as samples of plasma-treated silicon oxide, to identical TFMB solutions and choosing the concentration and exposure time that offered the largest observable difference between the two samples in the F 1s XPS signal intensity. Samples were sonicated in hexane for 5 min, rinsed sequentially with acetone and ethanol, and dried with flowing nitrogen. XPS measurements were taken using a monochromatic Al K α source, and data peaks were fit using Unifit XPS analysis software. High-resolution spectra were taken for a major core level of each respective element analyzed (F 1s, O 1s, N 1s), and results were quantified relative to other samples by dividing the integrated peak intensity of each respective element to the integrated Si 2p core level intensity. Measurements of surface roughness were collected using AFM in contact mode with gold-backed silicon nitride tips.

Protein Immobilization. Surfaces were prepared as described above and then exposed to a solution of 20% GA in Nanopure water for 2 h at room temperature. The GA solution was then aspirated, and the samples were exposed to a 2 mg/mL solution of NA in Nanopure water for 1 h at room temperature. Samples were then rinsed with water and dried with flowing nitrogen.

Radiolabeled Biotin Studies. For radiolabeling studies, ³H-labeled biotin was added at a concentration of 2 μ Ci/mL to a solution of non-labeled biotin at 7.25×10^{-7} g/mL in Nanopure water. Each sample size was measured with a micrometer to the nearest micrometer to determine surface area. Surfaces were incubated in the ³H-laden solution for 15 min at room temperature. After incubation, the surfaces were washed three times in Nanopure water and placed, functionalized side up, in the scintillation tube. A standard curve was prepared by serially diluting the initial spiked solution into Nanopure water at a 1:10 ratio. Background values were calculated from the label-free biotin stock. Scintillation fluid was added to bring all the samples to a fixed volume. The disintegrations per minute (DPM) were recorded for each sample and compared to the standard curve to establish a mass. The previously calculated area was used to determine the mass of biotin per area of surface.

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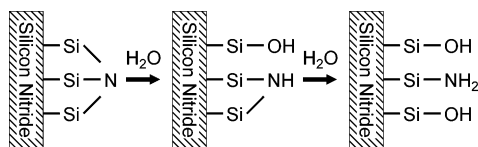


Figure 1. Schematic showing a pathway for the formation of primary amines on the surface of silicon nitride upon exposure to a humidified air plasma.

Values for a given sample were determined by averaging the mass per area for the individual samples. Significance was determined with a two-tailed Student's *t* test, and results that yielded a *P* value less than 0.05 were considered significant.

Fluorescent Assay. NA-coated surfaces were prepared as described above on silicon nitride-coated glass slides. A 1 μ L pipet was used to spot a 1 μ g/mL solution of biotinylated Atto-647 in water. The spot was incubated for 30 min at room temperature, and the slide was then immersed in a Petri dish containing a 1% solution of Tween-20 in water and placed on a rotator for 20 min. After this time, the slides were removed from the solution, rinsed with Nanopure water, and dried with flowing nitrogen. Glass control slides were exposed to identical surface preparation and cleaning methods. For fluorescent imaging, the slides were scanned at an excitation wavelength of 650 nm and imaged using commercial software.

Results and Discussion

Plasma Treatment. Low-temperature oxidation of silicon nitride was achieved by exposing samples to a radio frequency glow discharge plasma fed with low pressure air. The formation of amine groups during wet silicon nitride oxidation has been suggested previously^{21,24,32} and is thought to proceed through a mechanism similar to that shown in Figure 1. In our scenario, after exposure to the humidified plasma—which contains hydroxyl radicals and free hydrogen atoms, among other species—Si-N bonds are broken in favor of the more energetically favorable Si-O bonds, creating Si-NH and Si-OH on the surface. It should be noted, though, that while the schematic in Figure 1 is consistent with our data, it is not the only possible reaction scheme. The chemistry in plasma systems is very complex, and without the ability to directly monitor the chemistry in situ, we can only theorize as to the actual mechanism.

In order to track the formation of primary amines on the surface with sub-monolayer sensitivity, a more easily detectable label is required. Benzaldehydes are known to be specific labeling agents for primary amines,^{33–35} and by using a fluorinated compound such as TFMB for labeling (Figure 2, inset), an easily detectable XPS signal is obtained. Note that the F 1s core level peak at 689 eV associated with F-C bonds is easily distinguished from a smaller contamination peak at 685 eV associated with F-Si bonds that are incidentally created while cleaning with HF. The data presented in Figure 2 show measurements of the ratio of the F peak at 689 eV to total Si for a number of samples at varying plasma exposure times.

For the silicon nitride samples exposed to humidified plasma, a steady increase in TFMB binding is seen with increasing plasma exposure time. The TFMB uptake peaks at \sim 55 min and then rapidly declines. Similar behavior is *not* observed for silicon oxide samples, nor is it seen in the nitride samples exposed to dry plasma, which lacked a source of hydrogen needed to facilitate

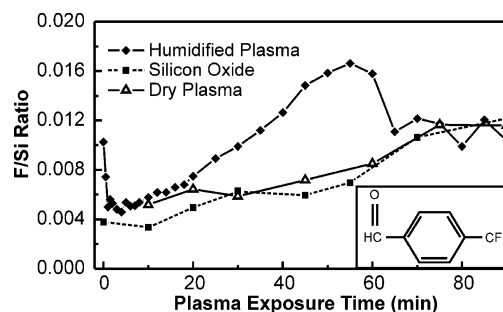


Figure 2. XPS analyses of the relative fluorine signal intensity versus plasma exposure for samples subsequently labeled with 4-(trifluoromethyl)benzaldehyde (TFMB). The signal is normalized to the Si 2p intensity. A distinct increase in TFMB binding can be seen for the nitride surfaces exposed to a humidified plasma, indicating the formation of surface amines. For silicon oxide samples treated with humidified plasma or dry-plasma treated nitride samples, only a slowly increasing nonspecific background signal is observed. Inset: the chemical structure of TFMB.

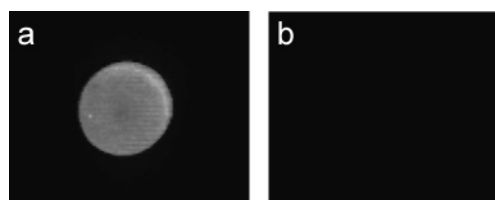


Figure 3. Fluorescent images of (a) a silicon nitride surface and (b) a silicon oxide surface spotted with 1 μ g/mL biotinylated Atto 647. Both surfaces were first exposed to a humidified plasma and then reacted with GA and NA as described in the text. The biotinylated fluorophore only binds to the nitride surface, indicating the specificity of the plasma treatment for creating functional amines.

amine formation. We attribute the observation of a nonzero “background” fluorine signal to a combination of nonspecific physisorption of TFMB onto the surface and the occurrence of a (much less favorable) side reaction of the benzaldehyde with surface hydroxyl groups. XPS has also shown that a small amount of carbonaceous contamination is added to the surface during the plasma treatment process in direct proportion to the plasma exposure time. This contamination may contribute to the slowly rising background signal by promoting nonspecific physisorption of the hydrophobic TFMB probe.

For practical purposes, we have found through various biomolecular assays (an example of which is shown in Figure 3) that no functional amines are created on silicon nitride in a dry plasma or on silicon oxide under any conditions we have examined. In Figure 3a, we show a humidified plasma-treated silicon nitride slide functionalized with GA and then NA, spotted with the fluorescent Atto 647-labeled biotin, and then rinsed. Figure 3b shows a silicon oxide slide subjected to the same treatment. The clear fluorescent spot seen in Figure 3a is in stark contrast to the essentially blank image in Figure 3b (protein functionalization will be discussed further in the next section.). It should be noted that at higher laser intensity, a faint spot can be seen on the silicon oxide control pictured in Figure 3b, but at these intensities, the corresponding signal for the silicon nitride sample is beyond the maximum limit for the detector, and hence a true visual comparison at this level cannot be made. This low level of binding is most likely due to a combination of nonspecific protein physisorption and the aldehyde side reactions mentioned in conjunction with Figure 2.

The mechanism underlying the formation and subsequent loss of surface amine groups on the plasma-treated nitride surfaces depicted in Figure 2 merits some further discussion. Figure 4

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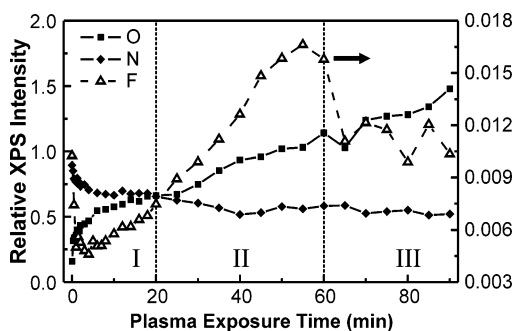


Figure 4. XPS analyses showing the relative amount of oxygen and nitrogen present at the nitride surface (left axis) after exposure to humidified plasma, overlaid with the TMFB fluorine signal intensities from Figure 2 (right axis). The relative XPS intensity is the ratio of the integrated peak intensity of each respective element (O, N, or F) to the integrated Si 2p core level intensity. Three regimes are observed, one at shorter times with rapid nitride oxidation and low concentrations of surface amines, one at intermediate times with a slower oxidation rate and high concentrations of surface amines, and one at long times, where the surface has effectively been converted to silicon oxide.

shows XPS data tracking the change in the oxygen and nitrogen content of the substrate, overlaid with the TFMB-binding data from Figure 2. There appears to be three roughly defined regimes. In the first regime, encompassing shorter exposure times up to ~20 min, there is a rapid increase in oxygen content and decrease in nitrogen content, with a modest amount of TFMB binding at time zero that drops to background levels almost immediately upon plasma exposure. In the second regime, encompassing intermediate exposure times from ~20 to 60 min, there is a significant decrease in the rate of nitrogen loss from the substrate and a gradual increase in TFMB binding, which reaches a maximum at ~55 min. In the final regime, for plasma exposure times > 60 min, the level of TFMB binding drops essentially to background levels as seen in Figure 2.

The intermediate and longer time regimes are relatively straightforward to interpret. At intermediate times, the reaction depicted in Figure 1 dominates, leading to the highest possible number of available surface amines. At longer times, the surface is oxidized such that the silicon nitride is buried under an oxide layer, so that the TFMB binding approximates that seen for a silicon oxide substrate. The data at shorter exposure times appear much more complex. Initially, there appear to be surface amines available for binding to TFMB; however, these are quickly depleted upon plasma exposure over roughly the same time frame of the most rapid nitride oxidation. It has also been found through numerous biomolecular assays that these initial amines will not stably immobilize biomolecules (data not shown). It would appear that if there are amines available at the nitride surface prior to plasma treatment, these amines immediately oxidize through hydrolysis when exposed to the humid plasma. We propose several possible contributing factors to this phenomenon. First, the rough grain structure of the sputter-coated nitride films may have a significant density of nonstoichiometric Si–N at the surface. Measurements of surface roughness taken with AFM show a decrease in rms roughness from 1.65 to 0.65 nm, a difference of 1.0 ± 0.3 nm, after 90 min of plasma exposure, indicating that asperities may preferentially react with the plasma. The potential role of defects near the surface of the silicon nitride matrix should also be considered. It has been noted in studies of the oxidation of CVD-grown bulk silicon nitride²⁵ that at low temperatures the rate of oxidation starts out slowly but gradually increases as more oxygen is incorporated into the atomic matrix. It was further noted that this oxidation did not occur at all without the presence

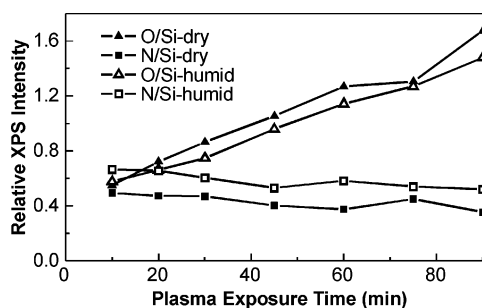


Figure 5. XPS analyses of the relative oxygen and nitrogen signal intensities versus plasma exposure time and plasma humidity for silicon nitride surfaces. Although Figure 2 indicates that surface amines are not created by the dry plasma, it is still effective at oxidizing the surface.

of a hydrogen source, such as water, leading the authors to theorize that the formation of Si–NH–Si sites is a required precursor to silicon nitride oxidation at low temperatures. If we examine the data in Figures 4 and 5, however, we find that this is not what we observe. Figure 4 clearly shows that the most rapid oxidation rate is seen at the shortest exposure times, while the data in Figure 5 indicate that—although we may not see primary surface amines on the dry-plasma treated samples—we definitely see significant oxidation. Both of these observations suggest our films start out with a significant density of Si–NH–Si defects near the surface. The difference in apparent oxidation rates may be due to differences between our sputter-coated samples and the CVD-grown samples used by Habraken et al. For example, the CVD films were much thicker than ours ($> 10\times$) and were characterized using less-sensitive methods. It is possible that our method of fluorine labeling and XPS analysis enables us to detect surface reactions that were actually present in the Habraken study but were not detectable using their methods (infrared and Auger electron spectroscopies). Finally, consideration should also be given to the potential role of Si–F bonds created during the initial cleaning with HF. Although this F is removed during the plasma treatment process, the unusually strong Si–F bonds may make adjacent Si–N bonds more susceptible to oxidation and thereby promote the reaction on our surfaces.

Biofunctionalization and Comparison to Silanes. We have used humidified plasma amination of silicon nitride as a starting point for covalent immobilization of functional protein films. Typically, surfaces have been treated with a solution of GA followed by attachment of a robust NA layer, similar to the surfaces in Figure 3. The NA-coated surface offers advantages such as the ability to attach biotinylated capture probes for biosensing (e.g., antibodies or oligonucleotides), as well as inhibition of nonspecific adsorption. Such functionalized surfaces have been successfully used for DNA hybridization assays and protein immunoassays in a variety of sample matrices, including whole blood, serum, plasma, urine, growth medium, and milk, with good repeatability and reliability.³⁶ Another potential application for this surface chemistry, as suggested by the results in Figure 3, is selective patterning of biomolecules through conventional lithography: because the chemistry affects nitrides but not oxides, surfaces could be patterned with nitride areas that could subsequently be selectively functionalized.

It is useful to compare our method with silane-based chemistries, which are the predominant methods for functionalizing silicon nitride, but can take hours to complete and generally require stringent atmospheric controls.^{3,5,6} Table 1 shows the

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Table 1. Reproducibility of Surface Amines for Plasma-Treated and Silane-Treated Surfaces

	av F/Si (<i>n</i> = 5)	std dev	% of av for 1 std dev
plasma	1.4×10^{-2}	0.1×10^{-2}	9%
silane ^a	15.5×10^{-2}	10.7×10^{-2}	69%

^a Numbers for silane film only include the 24% of samples that produced suitable monolayers.

average results for TFMB labeling for both plasma-treated and silane-treated silicon nitride surfaces and highlights the percentage of the total signal encompassed by a single standard deviation. The samples that were prepared using the humidified plasma treatment show excellent reproducibility, with one standard deviation representing only 9% of the total fluorine signal. Conversely, the silane-treated samples show a large degree of irregularity from one sample to the next, with one standard deviation representing 69% of the total fluorine signal. It should also be noted that the silane-treated nitride samples that were included in these statistics represent only 24% of the total samples that were initially prepared. Sixteen out of the 21 samples that were prepared with APTMS showed, upon examination with XPS prior to TFMB exposure, that either very little APTMS had been deposited (five samples), or that the APTMS had formed multilayers, resulting in a silane film that was so thick that it obscured the nitride surface from XPS analysis (11 samples). As mentioned in the Introduction, the formation of monolayers using silane chemistry can vary considerably with small changes in water content.^{11–13} The samples that were used to calculate the values in Table 1 were the five best samples, showing silane coverage somewhere between these two extremes. The five plasma-treated samples that were used were the first five that were prepared. The high degree of reproducibility seen in the plasma-treated samples allows for repeatable preparation of functionalized surfaces and highlights the difficulties of reproducibly preparing silane films with similar functionality.

Although the plasma-treated nitride surfaces are clearly more reproducible than those prepared with silanes, it is clear from Table 1 that silane functionalization creates a significantly higher density of surface amines. If we assume that the silanes create ~1 monolayer of amines, then the plasma treatment creates only about one-tenth of a monolayer. The effective density of protein immobilized to surfaces treated with both methods, however, is found to be comparable. The effective protein coverage was determined by functionalizing the surfaces with NA and then measuring the uptake of radiolabeled biotin. The results of these experiments are presented in Figure 6 and show that, despite a lower number of initial surface amines, the final degree of protein coverage for both methods is statistically equal, binding 1.4×10^{12} biotin molecules/cm². (Note that if functionalizing the surface with single-stranded DNA, this coverage is ideal for hybridization.³⁷) Assuming each NA occupies an area of ~25 nm² (4 nm × 5 nm × 5.6 nm),³⁸ an ideal, close-packed monolayer would be ~4 × 10¹² NA/cm². The actual density is likely to be lower, indicating that we are in the monolayer coverage regime. These results are consistent with previous studies³⁹ reporting that approximately complete protein monolayers can be formed on surfaces by functionalizing as little as one-tenth of the underlying

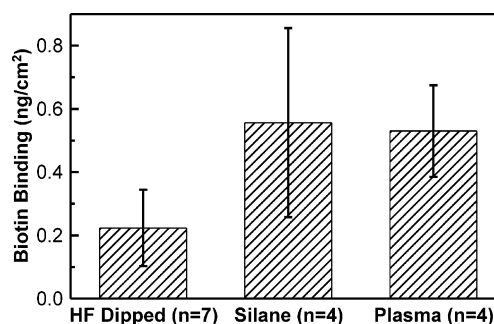


Figure 6. ³H-labeled biotin was used to estimate the surface uptake of biotin per square centimeter following different surface treatments. Both the silane and plasma-treated samples bound a concentration of ³H-biotin significantly greater than the controls (simply cleaned in hydrofluoric acid), with *P* values of 0.026 and 0.004, respectively. The biotin concentrations on the silane and plasma treated surfaces was not significantly different (*P* value of 0.88). Data are presented as the average of *n* samples, with the error bars showing the standard deviation.

surface with active binding sites. Thus, we find that when directly comparing our plasma treatment with silane-based methods, our approach enables comparable functionalization while being both more reproducible and relatively problem-free.

Finally, it is important to note that the method described here should be applicable to other nitride surfaces that can be oxidized in a humid plasma, including metal nitrides and III–V semiconductor nitrides. We have preliminary data (not shown) demonstrating that such treatment of gallium nitride also produces surface amines that can be used for subsequent functionalization and that the resulting surfaces are robust in biomolecular assays. Our results indicate that the density of amines produced is inversely proportional to the enthalpy of oxidation of the substrate, but more materials must be examined to definitively establish this trend.

Conclusions

We have developed a silane-free method for directly functionalizing silicon nitride with primary amines. The amines are created by exposing the surface to a radio frequency glow discharge plasma fed with humidified air. Surface amines are not similarly created on silicon oxide surfaces treated with humidified plasma or on nitride surfaces using dry air plasma. We have used the amines so created to subsequently functionalize silicon nitride surfaces with NA using GA as a bifunctional linker, and a number of biomolecular assays have been successfully performed using the resulting surfaces. When compared directly to silane-based methods, we find that the plasma-aminated nitride surfaces offer an identical final protein coverage but notably better reproducibility. This approach should be of utility for biosensors and bioMEMS devices where silicon nitride films are commonly used (or can be easily added) as a terminal passivation layer. It also is extensible to other nitride substrates.

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